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THE COMPRESSIBILITY MEASUREMENTS ON LIQUIDS

By Ryo Kiyama, Hiroshi Teranishi and Kazuo Inoue

Introduction

In a high pressure apparatus, water, mercury, alcohols, glycerin, machine oils, and silicone oils, etc. are used as pressure transmitting liquids. It is desirable that in order to be used as the transmitting liquids, the liquids have the following properties,—(a) they are chemically stable, (b) the changes of their viscosities by temperature are small, (c) their melting points under pressures are below, and (d) their physical constants under a wide range of pressure and temperature have been elucidated. Water, mercury, alcohols, and glycerin, whose physical constants under pressures have been measured, have the faults for use due to their low melting points under high pressures or chemical stabilities. The viscosities of machine oils have wide difference according to their kinds, and change widely by temperature, and the compressibilities of the oils have not been reported in literature. Silicone oils are chemically stable, their flash points are about 315°C and the changes of their viscosity by temperature are smaller than those of machine oils, but their compressibilities have not been reported in literature except P. W. Bridgman's report[1] (published during the present measurements) in which, however, the differences of two neighbouring pressures observed are too wide, and the experimental temperatures have not been described. Therefore, in order to measure the compressibilities of machine oils and silicone oils, the authors have constructed the two apparatus for compressibility measurement on liquids, the one for lower pressure ranges and the other for higher, both of which are able to be employed under the pressures changing continuously. The former by which H. Teranishi has measured the results in Part I, has a modified type of E. P. Perman and W. D. Urry's apparatus employed in 1930[2], and can be used for viscous liquids, the latter, by which K. Inoue has measured the results in Part II with assistance of Mr. K. Ozawa, has a modified type of F.G. Keyes' reported in 1933[3], and can measure directly the volume change of the sample independent of that of mercury.

The compressibility k of liquid is defined as the following equation[4],

$$k = -\frac{1}{V_1} \times \frac{V_2 - V_1}{P_2 - P_1}$$

where V_1 and V_2 are the volumes of liquid under the pressures P_1 and P_2 respectively.

1) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, 77, 115, 129 (1949)
2) E. P. Perman and W. D. Urry, *Proc. Roy. Soc.*, 126, 44 (1930)
3) F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, 68, 505 (1933)
4) Landolt-Börnstein, "*Physikalisch-chemische Tabellen*," (5 Auflage) I, 94 (1923)

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In this work, P_1 is always 1 atm[5] and so k means the average compressibility under the pressure range from 1 to P_2 atm.

The distilled water, which had been boiled to remove the bubbles contained, was employed in the calibrating tests of both apparatus[6].

For the compressibility measurements of machine oils, three kinds of Mobil oils A, BB, and B (S. A. E. 30, 50, and 60 respectively) of Standard Vacuum Oil Co., N. Y., preceding the measurement on home products, were employed, after the bubbles contained had been removed by heating to 80°C for 1 hour.

For silicone oil, the samples of two groups (a) and (b) were employed. The oils of (a) were synthesized, separated, and purified in our laboratory by T. Ikegami and T. Izumitani in 1949[7] as described below. Methyl chlorosilanes, which were produced by the reaction of methyl chloride and sintered metallic silicon-cupper mixture at 285°C, were distillated by means of a Podbielniak's distillator and dimethyl dichlorosilane (B. P. 70.2°C) was separated. Then the latter was dissolved in the same volume of ethyl ether and an ether solution was hydrolized by being added dropwise to the same amount of water at 0°C. The products were distillated by means of a Podbielniak's distillator and the sample oils were separated at the conditions described below.

Molecular form	*Molecular weight*	*Boiling point*
$[(CH_3)_2SiO]_4$	296	74.5 ~ 76.0°C (19~20 mm Hg)
$[(CH_3)_2SiO]_5$	370	92.0 ~ 100.5°C (20 mm Hg)

Four oils of group (b) were high polymers of dimethylsiloxane* signed SS-I, -II, -III, and -IV respectively in order of their viscosities, and the following table shows their densities and viscosities at 20°C and the average molecular weights[8] which were determined by the measurements of viscosities of their toluene solutions.

	Average molecular weight	*Density* (20°C) g/cc	*Viscosity* (20°C) c.s.
SS-I	1130	0.940	10.4
SS-II	6800	0.961	100
SS-III	13900	0.971	272
SS-IV	43000	0.974	4530

PART I

Experimental Apparatus and Procedures

In the E. P. Perman and W. D. Urry method[2], the sample liquid is filled in a capillary glass piezometer which has a dilated part at one end. The dilated part is set in a steel

5) L. B. Smith and F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, 69, 313 (1934)
6) E. H. Amagat, *Ann. Chim. Phys.*, (6) 29, 68, 505 (1893)
7) R. Kiyama, T. Ikegami and T. Izumitani, *Unpublished.*
8) A. J. Barry, *J. App. Phys.*, 17, 1020 (1946)
* Donated by Shin-etsu Chem. Ind. Co., Tokyo.

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vessel and protected for destruction by pressure, and the other end of the piezometer is connected with a steel pipe. The volume changes of the sample liquid due to pressures are read from displacements of the head of the sample liquid which contacts in the capillary part with pressure transmitting mercury. By this method, when the sample liquid becomes viscous, the volume change of the sample would be inaccurate, because a part of the sample which adheres on the inner wall of the piezometer would be enclosed in the mercury part by displacements of the mercury head. To improve the flaw, in the authors' method, mercury is filled in a piezometer together with the sample liquid, and the volume changes due to pressures are read from displacements of the mercury head which contacts in the capillary part with pressure transmitting air. Besides, considering the simplicities of washing the piezometer and of sampling, and the certainties of removing fine bubbles on the inner wall of the piezometer and of the jointing of glass to steel, the authors have constructed the apparatus described below in detail.

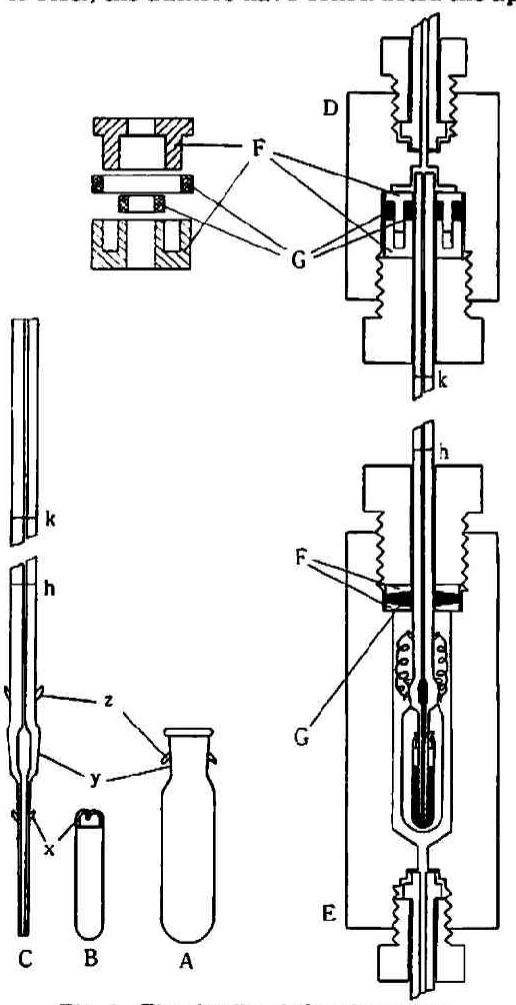

Fig. 1 The details of the piezometer and the glass-steel joints

The details of the piezometer and of the methods of glass-steel joints are shown in Fig. 1. The piezometer consists of a sample vessel A, a mercury vessel B, and a capillary glass C. A is about 6 cc and B is about 1.5 cc in capacity respectively, C is 0.8 cm and 0.087~0.113 cm in outer and inner diameters respectively, and 35 cm in length and the observable part in the experiments (between the marked lines, h and k) is 17 cm in length. After the capillary glass C is annealed at 500° C, and quenched if necessary, the capacities of the observable part and of the whole piezometer are measured by weighing the mercury stuffed in them. For sampling the piezometer, the vessel B is filled with the mercury, whose quantity has been precisely measured, and is hung from C by the projections x and then B and C are sunk into the vessel A which has been filled with the sample liquid, and the glass joint part y is fixed, and the projections z of A and C are fastened with spring wires. When the glass joint part y is fixed, the sample liquid is compressed and mercury in the

vessel B rises inside the capillary glass C and the head of mercury comes to the observable part. The piezometer is then jointed to steel pipes at the upper and lower parts in steel vessels D and E respectively. Both joints are the self-tightening systems consisting of steel rings F and rubber rings G[9,10]. The lower joint is tightened first, and then the upper one by hand. Both joints are more tightened automatically by pressure elevations, and neither, of course, pressure leak nor destruction of glass are observed in these joints. The vessels D and E are fixed to an iron stand in a thermostat.

The pressure transmitting apparatus is shown in Fig. 2. V's are high-pressure valves, and by the air bomb R and the intensifier T the pressure is adjusted to a desired value. A pressure gauge P of Bourdon type has been graduated at 1/3 kg/cm² from 0 to 100 kg/cm² and tested by means of a dead weight tester. Each experimental temperature is kept constant within the fluctuation of ±0.01°C in a water thermostat.

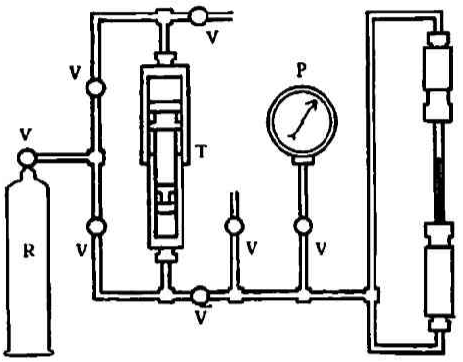

Fig. 2 The pressure transmitting part of the apparatus

The volume of the sample liquid at 1 atm is determined by reducing the volume of the mercury employed from the capacity of the piezometer and correcting the volume change caused by the pressure which is exerted by the height of mercury in the piezometer. The volume changes of the sample liquid due to applying pressures are determined by reducing the volume change of mercury[5] from the volume change corresponding to the displacement of the mercury head which can be read to 1/100 mm by means of a cathetometer.

Results

Table 1
The compressibilities of water

P atm	$k \times 10^7$ 20°C
1— 9.82	492
〃 15.83	491
〃 22.02	487
〃 28.36	485
〃 34.63	484
〃 40.92	481
〃 47.21	479
〃 53.50	476
〃 59.79	475
〃 66.08	474
〃 72.37	473
〃 78.66	473
〃 84.96	472
〃 91.25	471

(1) Water

The results of compressibility measurements at 20°C are shown in Table 1. The compressibility values k are the average values between 1 atm and the pressures listed in the first column. The results coincide with Amagat's data[6] within experimental errors.

(2) Mobil oils

The results of measurements at 20°, 30°, and 40°C are shown in Table 2. In each sample, the compressibilities become larger as temperature becomes higher,

9) R. Kiyama and K. Inoue, *This Journal*, **21**, 74 (1951)
10) R. Kiyama, K. Suzuki and T. Ikegami, *ibid.*, **21**, 54 (1951)

and at each temperature the compressibilities become smaller as the viscosities of oils become larger.

Table 2 The compressibilities of Mobil oils

Mobil oil A				Mobil oil BB				Mobil oil B			
P	$k \times 10^7$			P	$k \times 10^7$			P	$k \times 10^7$		
atm	20°C	30°C	40°C	atm	20°C	30°C	40°C	atm	20°C	30°C	40°C
1~15.87	594	630	668	1~15.87	588	623	659	1~15.83	577	610	644
〃 22.08	588	625	659	〃 22.08	582	613	646	〃 22.04	575	600	632
〃 28.35	583	622	652	〃 28.35	578	608	638	〃 28.31	566	597	629
〃 34.64	578	618	649	〃 34.64	573	606	635	〃 34.60	563	595	623
〃 40.93	575	615	648	〃 40.93	570	603	633	〃 40.89	559	592	621
〃 47.21	572	613	646	〃 47.11	567	600	631	〃 47.17	557	588	619
〃 53.51	571	611	641	〃 53.51	565	599	628	〃 53.47	556	587	618
〃 59.80	571	609	640	〃 59.80	564	598	627	〃 59.76	555	586	617
〃 66.09	571	609	640	〃 66.09	564	597	626	〃 66.05	553	585	616
〃 72.36	570	608	640	〃 72.36	561	597	624	〃 72.32	548	585	614
〃 78.69	569	605	639	〃 78.93	560			〃 78.64	548	584	614

(3) Silicone oils

The results of experiments at 20°, 30°, and 40°C are shown in Table 3. In each sample, as in the case of Mobil oils, the compressibilities become larger as temperature becomes higher, and at each temperature, the values become smaller as the molecular weights and viscosities become larger.

Table 3 The compressibilities of silicone oils

$[(CH_3)_2SiO]_4$				$[(CH_3)_2SiO]_5$				SS-1			
P	$k \times 10^7$			P	$k \times 10^7$			P	$k \times 10^7$		
atm	20°C	30°C	40°C	atm	20°C	30°C	40°C	atm	20°C	30°C	40°C
1~ 9.81	1556	1717	1850	1~ 9.78	1348	1465	1580	1~ 9.86	1218	1290	1420
〃 15.82	1480	1634	1795	〃 15.79	1310	1433	1543	〃 15.87	1206	1266	1371
〃 22.01	1431	1591	1725	〃 21.98	1280	1401	1515	〃 22.06	1172	1251	1342
〃 28.35	1399	1551	1686	〃 28.32	1249	1376	1491	〃 28.40	1157	1232	1329
〃 34.62	1374	1517	1664	〃 34.59	1240	1362	1475	〃 34.67	1145	1222	1320
〃 40.91	1371	1511	1658	〃 40.88	1233	1339	1466	〃 40.96	1139	1216	1316
〃 47.20	1363	1489	1634	〃 47.17	1219	1326	1452	〃 47.25	1130	1208	1309
〃 53.49	1349	1485	1627	〃 53.46	1208	1323	1442	〃 53.54	1124	1200	1303
〃 59.78	1336	1481	1622	〃 59.75	1206	1315	1430	〃 59.83	1121	1197	1299
〃 66.07	1334	1475	1616	〃 66.04	1201	1310	1422	〃 66.12	1118	1191	1292
〃 72.36	1331	1467	1607	〃 72.33	1195	1304	1417	〃 72.41	1116	1185	1287
〃 78.65	1327	1465	1600	〃 78.62	1190	1300	1406	〃 78.70	1113	1184	1284
〃 84.95	1320	1450		〃 84.92	1176	1295		〃 85.00		1179	1281
				〃 91.21		1290					

(Table 3 *continued*)

SS-II				SS-III				SS-IV			
P atm	$k \times 10^7$ 20°C	30°C	40°C	P atm	$k \times 10^7$ 20°C	30°C	40°C	P atm	$k \times 10^7$ 20°C	30°C	40°C
1~ 9.85	1190	1234	1335	1~ 9.90	1140	1231	1290	1~ 9.88	1130	1210	1252
〃 15.82	1152	1231	1319	〃 15.91	1128	1202	1275	〃 15.83	1120	1197	1242
〃 22.12	1141	1213	1302	〃 22.10	1116	1187	1266	〃 22.14	1100	1174	1217
〃 28.39	1127	1206	1277	〃 28.44	1107	1168	1251	〃 28.40	1086	1163	1205
〃 34.67	1118	1197	1269	〃 34.71	1098	1159	1242	〃 34.68	1082	1149	1197
〃 40.97	1111	1191	1260	〃 41.00	1094	1153	1236	〃 40.98	1079	1144	1191
〃 47.25	1106	1187	1258	〃 47.29	1090	1148	1232	〃 47.26	1075	1136	1189
〃 53.55	1102	1183	1255	〃 53.58	1087	1144	1231	〃 53.56	1073	1134	1187
〃 59.84	1098	1180	1252	〃 59.87	1085	1142	1230	〃 59.85	1070	1133	1185
〃 66.13	1097	1178	1250	〃 66.16	1084	1139	1227	〃 66.14	1068	1128	1183
〃 72.40	1096	1176	1249	〃 72.45	1083	1135	1225	〃 72.42	1066	1124	1181
〃 78.72	1092	1174	1244	〃 78.74	1081	1134	1221	〃 78.73	1061	1120	1180
				〃 85.04	1077	1129	1217	〃 85.03	1059		

Pressure is read by means of the pressure gauge graduated at 1/3 kg/cm², and the volume change is measured, involving the error due to the temperature fluctuations, in accuracy of ±3/100 mm in the displacement of mercury head in the piezometer. The error in the measurement of the capacity of the piezometer and that due to the expansion by internal pressure[2] of the capillary part, which is exposed to atmospheric pressure, are negligible as compared with the error mentioned above.

The errors of the compressibility values which are calculated[11] from those concerning the measurements of temperature, pressure and volume, are about 2.0 and 0.19 % at 9.82 and 91.25 atm respectively for water, 4.4 and 0.28 % at 15.83 and 78.93 atm respectively for Mobil oils, and 3.6 and 0.10 % at 9.88 and 85.00 atm respectively for silicone oils.

PART II

Experimental Apparatus and Procedures

The piston displacement method is used in this experiment. The layout of the apparatus is shown in Fig. 3. The vessel C of the high pressure volumenometer is made of special steel and is 50 mm in external diameter, 180 mm in length and is applicable up to a few thousands atmospheres. It consists of a wide part which is 20 mm in internal diameter and 20 cc in volume, and a narrow cylinder part to be fitted to the piston P. The piston is made of special steel, and 8 mm in diameter, 80 mm in length, and is ground in the same way as the cylinder. A self-tightening packing[12] is used on the piston head H, and the steel rod S fixed to the piston head is observable and the displacement

11) R. Livingston, "*Physico Chemical Experiments*," p. 21 (1939) Macmillan Co.
12) R. Kiyama, *This Journal*, 19, 5 (1945)

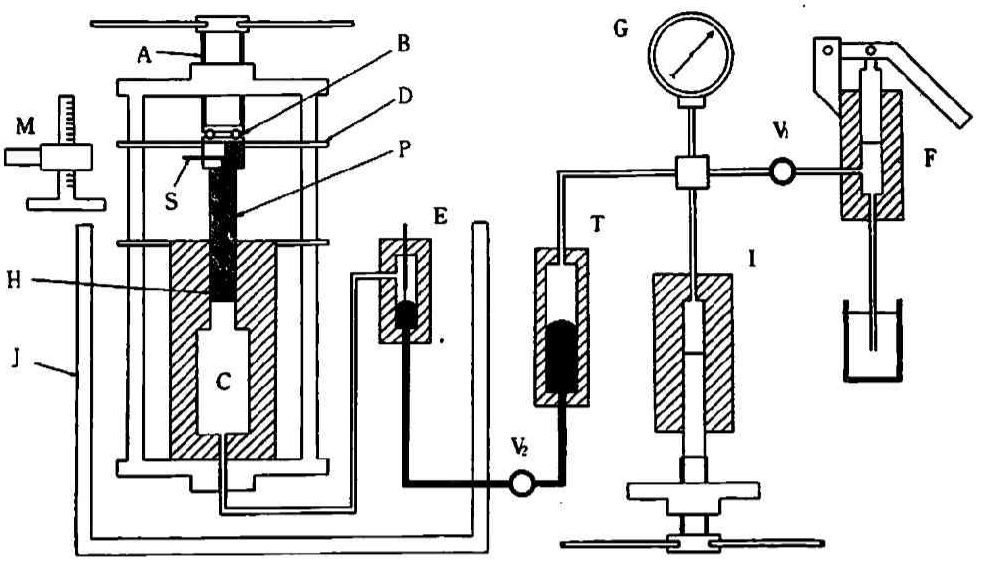

Fig. 3 The measurement apparatus

of the position of the rod is measured by the cathetometer M graduated at 0.01 mm, in order to measure the height of the piston head regardless of the change of the thickness of packing due to deformation by pressure. The piston is thrust by four handles fixed to the screwed rod A, and to prevent the rotation of the piston, the thrust bearing B and the steel plate D are used.

The mercury head contacting with the sample, is kept at constant level by the electrode E, which has the same mechanism as reported [13]. In the measurements on water and oils, a nickel and a hardened steel rods are used as a contacting lead wire respectively. To prevent the chemical change and the emulsification of the sample and mercury, the amount of the current is decreased as small as possible by using the vacuum tube circuit. The height of mercury head in E is controlled by means of the intensifier I, with which E is connected through the trap T by pressure transmitting oil. The intensifier consists of a piston and a cylinder, 10 mm in diameter, and pressure is applied to transmitting oil by the same handling as in the case of the volumenometer. F, G and V show a hand pump, a Bourdon type pressure gauge and a high pressure valve respectively. Every part, to which pressure is applied, is connected with each other by steel tubes, 8 mm in external and 1 mm in internal diameter.

As to the operation, the piston and the electrode are taken away, and the sample is filled in the volumenometer and the electrode vessel keeping the height of mercury head in the electrode vessel near the working point of the electrode by closing the valve V_2. After the electrode is set and V_2 is opened, the piston is fitted in the cylinder controlling the height of mercury head. Then V_1 is opened and the pressure transmitting oil, compressed preliminaryly by the hand pump, is led to the intensifier. Afterwards, V_1 is

13) R. Kiyama, *This Journal*, 19, 13 (1945)

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closed, and pressure is applied by driving the screwed parts of the volumenometer and the intensifier at the same time in order to keep constant the height of mercury head. The compressibility measurements are started from 88 atm, because the self-tightening packing does not work under the lower pressure.

In the pressure measurements, three pressure gauges of Bourdon type, calibrated by a dead weight and a standard Bourdon type pressure gauges, are used. The maximum pressures of their gauges are 300, 1000 and 2000 kg/cm^2, and graduated at 1, 20 and 50 kg/cm^2 respectively. The first has the accuracy of one tenth of a graduation by the reflection of a mirror, and the latter two have that of one third.

The total volume of the volumenometer, the electrode vessel and their connecting tube is determined by weighing the mass of mercury which is filled in them. The measured volume under pressure is corrected with the volume change due to the deformation of the vessels to which the pressure is applied.

The sampling parts C and E are set in the thermostat J and the temperature is measured in accuracy of 0.05°C by means of a standard mercury thermometer. The pressure is applied slowly in order to keep the balance of temperature, and the volume is measured after making sure that the volume does not change at a given pressure.

Results

(1) Water

The compressibilities of water up to a pressure of 1500 atm at 20° and 30°C are

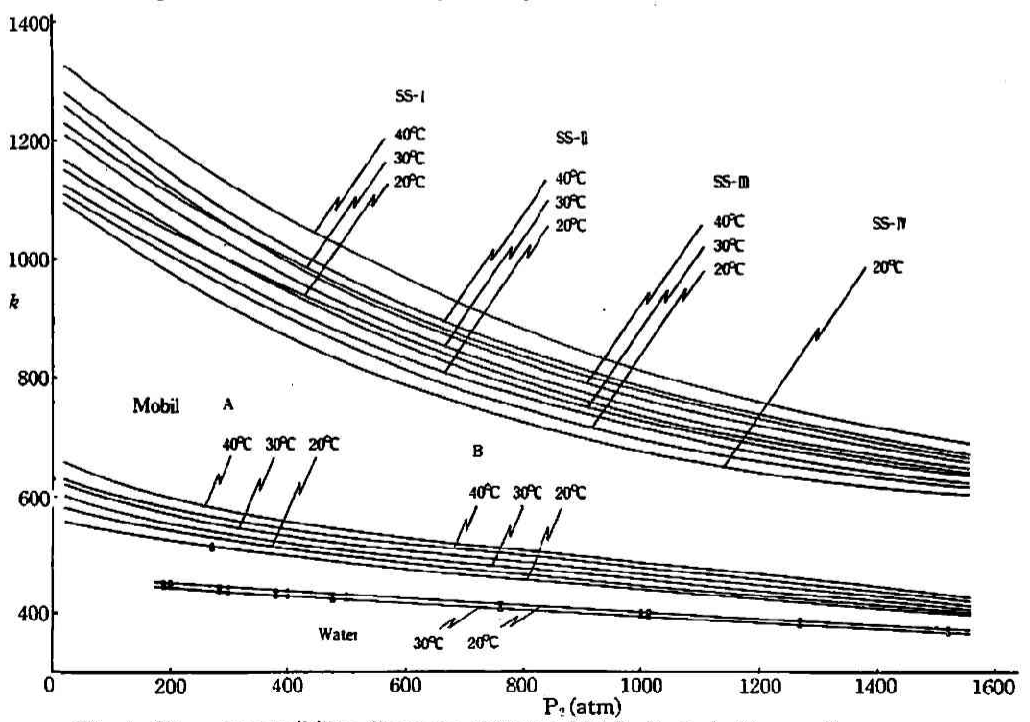

Fig. 4 The compressibility diagrams of water, Mobil oils and silicone oils
× Amagat ○ Authors

measured in order to certificate the apparatus, and compared with Amagat's data[6]. Amagat's values in Table 4 and Fig. 4 are calculated from his reported values to be compared with our data. The compressibility values k are the average values from 1 atm to the pressures listed in the first column in tables.

Table 4 The compressibilities of water

Authors			Amagat		
P atm	$k \times 10^7$ 20°C	30°C	P atm	$k \times 10^7$ 20°C	30°C
1 ~ 187	452	447	1 ~ 200	454	447
〃 284	445	438	〃 300	446	437
〃 380	438	430	〃 400	439	430
〃 477	432	424	〃 500	434	424
〃 761	417	406	〃 750	—	—
〃 1014	401	393	〃 1000	403	395
〃 1269	390	380	〃 1250	—	—
〃 1525	375	370	〃 1500	377	—

(2) Mobil oils

In three kinds of Mobil oils, the compressibilities of Mobil A and B are measured from 88 atm up to 1500 atm at 20°, 30° and 40° C, and calculated the average compressibilities from 1 atm to the pressures listed, using the data of Part I. The results are shown in Table 5 and Fig. 4.

Table 5 The compressibilities of Mobil oils

P atm	Mobil oil A			Mobil oil B		
	$k \times 10^7$ 20°C	30°C	40°C	20°C	30°C	40°C
1 ~ 187	545	574	600	529	557	583
〃 284	530	552	580	514	537	564
〃 380	516	539	563	503	526	548
〃 477	500	523	549	490	513	536
〃 761	470	490	512	460	477	505
〃 1014	445	466	485	440	458	477
〃 1269	425	441	458	418	434	451
〃 1525	407	420	431	404	414	424

(3) Silicone oils

The compressibilities of SS-I, SS-II and SS-III at 20°, 30° and 40° C, and SS-IV at 20° C are measured from 88 atm up to 1500 atm and calculated the average compressi-

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bilities from 1 atm to the pressures listed, using the data of Part I. The results are shown in Table 6 and Fig. 4.

Table 6 The compressibilities of silicone oils

P atm	$k \times 10^7$									
	SS - I			SS - II			SS - III			SS - IV
	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C	20°C
1~ 187	1057	1118	1198	1030	1094	1153	1010	1061	1130	990
〃 284	1006	1060	1134	979	1034	1085	963	1003	1062	930
〃 380	962	1010	1074	930	980	1030	908	951	1009	881
〃 477	915	961	1026	883	932	979	861	905	955	836
〃 761	804	847	896	780	818	859	759	793	837	736
〃 1014	732	771	810	713	748	781	692	726	758	674
〃 1269	680	715	745	663	692	725	650	675	705	632
〃 1525	642	666	695	625	649	676	616	638	661	605

The errors of compressibility values which are calculated[11] from those concerning the measurements of temperature, pressure and volume, are about 0.60 and 0.36 % at 187 and 1525 atm respectively for water, 0.58 and 0.36 % for Mobil oils and 0.41 and 0.37 % for silicone oils.

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